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The Crystal Structure of Tetramethylammonium Diisocyanatoargentate(I)

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The crystal structure of tetramethylammonium diisocyanatoargentate(I), $(CH_3)_4NAg(NCO)_2$, has been determined by three-dimensional X-ray diffraction methods. The crystals are orthorhombic, space group *Pnma* (No. 62), with cell dimensions $a = 10.867(6)$ Å, $b = 6.614(5)$ Å, and $c = 13.852(7)$ Å. Intensity data were collected with an automatic single-crystal diffractometer, using Nb-filtered Mo$K\alpha$ radiation. Least squares refinement, based on 640 independent, non-zero reflections, resulted in a conventional R value of 0.048.

The crystals contain diisocyanatoargentate(I) ions and tetramethylammonium ions. The approximately linear $[OCNAgNCO]^-$ ions are located in mirror planes. The Ag—N bond lengths are 2.015(13) and 2.068(12) Å, and the N—Ag—N bond angle is 177.2(5)°. The tetramethylammonium ions also possess mirror plane symmetry. They are subject to disorder or extreme thermal motion, with rotation about one of the N—C bonds.

The synthesis of tetramethylammonium diisocyanatoargentate(I), $(CH_3)_4NAg(NCO)_2$, has been reported earlier.[1] From vibrational spectra it has been deduced that the crystals contain complex anions $Ag(NCO)_2^-$ with a symmetry centre, and with the silver atom bonded to the nitrogen atoms of the pseudohalide groups.[2] In conformance with the vibrational spectra, a ^{14}N NMR study has shown that the NCO groups are nitrogen-bonded in this compound.[3] The crystal structure has now been determined by X-ray diffraction methods, and is reported here.

EXPERIMENTAL

Collection of X-ray data was done by means of a Siemens automatic, off-line, single-crystal diffractometer (AED), using Mo$K\alpha$ radiation (Nb-filtered). The diffractometer was operated as a three-circle instrument.

The measurements were performed on a crystal with the following dimensions, given as distances from a common origin to faces: Distances to (001) and $(00\bar{1}) = 0.25$ mm; to (101) and $(\bar{1}0\bar{1}) = 0.22$ mm; to $(10\bar{1})$ and $(\bar{1}01) = 0.21$ mm; and to (011), $(0\bar{1}\bar{1})$, $(01\bar{1})$, and $(0\bar{1}1) = 0.24$ mm. The crystal was mounted with the c axis approximately along the ϕ axis of the diffractometer, and its orientation and cell dimensions were determined by measuring the θ, χ, and ϕ angles for five non-coplanar reciprocal vectors. Intensity data were collected with a scintillation counter, using the $\theta - 2\theta$ scan technique. The scan-speed was set to 5-degrees per minute in the θ angle, with automatic setting of twice this speed for strong reflections. The rather high scan speed was chosen because of rapid blackening of the crystal when exposed to air and X-rays. Counting losses were avoided by means of attenuation filters, which were automatically inserted into the primary beam when needed. Each reflection was scanned between $\theta_1 = \theta - 0.40°$ and $\theta_2 = \theta + 0.40° + 0.35° \operatorname{tg} \theta$, where θ is the Bragg angle for the α_1 peak. The scan was carried out by going from θ to θ_1, then from θ_1 to θ_2, and finally from θ_2 to θ. The intensities over each scanning range were recorded at the end of each step. The background was measured for one half of the total scan time at θ_1 and one half at θ_2. The intensities of all independent reflections with $\theta \leqq 25°$ were measured.

Using the intensity variations of two reference reflections, measured at intervals of 50 reflections, the net intensities were brought to a common scale. The lower limit for an observed reflection was set equal to two times the standard deviation in net intensity. The standard deviation in net intensity is $(I_t + I_b)^{\frac{1}{2}}$, where I_t is the total intensity, and I_b is the background intensity. Out of 966 measured reflections, 640 had intensities above the lower limit. The remaining 326 reflections were assigned an intensity equal to the observable limit, and la-

belled as unobserved reflections.

The intensities were corrected for absorption ($\mu = 19.4$ cm^{-1}), using a modified version of the correction method originally described by Busing and Levy.[4] A $10 \times 10 \times 8$ grid was applied in the calculations. Lorentz and polarization corrections were carried out, and the corrected intensities were reduced to relative observed structure factors.

The calculated structure factors were based on the atomic scattering factor curves listed in *International Tables*.[5] Using the $\Delta f'$ and $\Delta f''$ values given by Cromer,[6] the silver scattering curve was corrected for anomalous dispersion, by taking the amplitude of f as the corrected value.

Least squares refinement was carried out with a full-matrix program minimizing the function

$$r = \sum W(|F_o| - K|F_c|)^2$$

where K is a scale factor, and the weight, W, is the inverse of the variance in F_o. The variance in F_o is

$$\sigma^2(F_o) = F_o^2[I_t + I_b + k^2(I_t - I_b)^2]/4(I_t - I_b)^2$$

where k may be interpreted as the relative standard deviation in the scaling curve. The value of k was estimated to be 0.02. Non-observed reflections for which $K|F_c|$ is greater than the observable limit, are included in the refinement with $|F_o|$ equal to the observable limit.

The calculations were carried out on an IBM 360/50 H computer. Most programs used have been listed in an earlier paper.[7] Rigid-body motion analysis was carried out with the program RBM, written by Schomaker and Trueblood,[8] and adapted for the IBM computer by L. Milje, of this Institute. A drawing was performed with the program OR TEP, written by C. K. Johnson.[9]

CRYSTAL DATA

The crystals of tetramethylammonium diisocyanatoargentate(I) occurred as colourless, orthorhombic prisms bounded by {001}, {101}, and {011}. Calculations of unit cell dimensions by a least squares procedure were based on 10 high-angle θ-values measured on the diffractometer. The numbers in parentheses are standard deviations in last digits:

$a = 10.867(6)$ Å; $b = 6.614(5)$ Å; $c = 13.852(7)$ Å; $V = 995.6(11)$ Å^3; $M = 266.05$; $F(000) = 528$; $Z = 4$;

ϱ_o(flotation) $= 1.775$ g/cm^3; $\varrho_c = 1.774$ g/cm^3.

Systematic absences are $0kl$ when $k + l = 2n + 1$, and $hk0$ when $h = 2n + 1$. The space group is either $Pna2_1$ (No. 33) or $Pnma$ (No. 62). (Most data quoted here were reported in the earlier paper.[1])

STRUCTURE DETERMINATION

A test for centrosymmetry was made by applying the method of Foster and Hargreaves [10] to the intensities, but no definite conclusion could be reached. No further attempts were made to distinguish between the two possible space groups at this stage.

As both space groups have centrosymmetric $h0l$ projections (indexing according to space group $Pnma$), this projection was first examined. A Patterson synthesis readily gave the x and z coordinates of the silver atom. Most of the lighter non-hydrogen atoms were located through subsequent Fourier syntheses. Only the nitrogen atom [N(3)] and one methyl carbon atom [C(3)] of the tetramethylammonium ion showed up as distinct peaks in the maps. This was thought to be due to disorder of the remaining methyl carbon atoms.

From the positions of the atoms in the $h0l$ projection, and assumed bond lengths, the centrosymmetric space group $Pnma$ appeared to be the most probable one, and the three-dimensional structure analysis was therefore based on this space group. The determination of the y coordinates offered no problem, since most of the atoms, including the silver atom, has to be situated in mirror planes normal to the b axis. The disorder of the methyl carbon atoms showed up in the three-dimensional Fourier maps as well, no matter whether these atoms had been included in the preceding structure factor calculations or not. The disorder might be described as a 60° rotation of the tetramethylammonium ion about one of the nitrogen-carbon bonds, N(3)–C(3), transferring the three other methyl carbon atoms of the ion from one set of positions to another. Two requirements have to be imposed on the occupancy factors when this model is applied. The occupancy factors have to be equal within each set of positions (leaving out of account the factor of 0.5 for atoms situated in mirror planes). Also, the sum of occupancy factors have to make up one tetramethylammonium ion. The least squares program used for refinement of

Table 1. Atomic coordinates in fractions of orthorhombic cell edges, and occupancy factors. Standard deviations from the least squares refinement in parentheses.

	x	y	z	Occupancy
Ag	0.03938(8)	0.25	0.07657(6)	0.5
N(1)	−0.1152(12)	0.25	−0.0039(9)	0.5
C(1)	−0.2059(14)	0.25	−0.0351(10)	0.5
O(1)	−0.3058(9)	0.25	−0.0723(7)	0.5
N(2)	0.2029(10)	0.25	0.1530(9)	0.5
C(2)	0.2972(13)	0.25	0.1843(10)	0.5
O(2)	0.3932(11)	0.25	0.2157(9)	0.5
N(3)	0.1458(7)	0.75	0.3517(5)	0.5
C(3)	0.2778(11)	0.75	0.3333(11)	0.5
C(4)	0.0811(21)	0.75	0.2539(14)	0.278(9)
C(5)	0.1197(21)	0.9289(29)	0.4061(17)	0.556(15)
C(6)	0.1189(28)	0.75	0.4635(18)	0.222(9)
C(7)	0.0838(23)	0.9336(38)	0.3163(25)	0.444(16)

structural parameters did not contain options for these requirements, and the occupancy factors therefore had to be adjusted after each cycle in which they had been subject to refinement. The initial values of the occupancy factors were estimated from the relative hights of the corresponding peaks in the electron density map.

The three-dimensional least squares refinement was started with individual isotropic thermal parameters. After a series of cycles, including one refinement cycle on the occupancy factors of the disordered carbon atoms, the conventional R value was 0.119. Anisotropic thermal parameters were introduced for the atoms of the diisocyanatoargentate ion, and the refinement was continued to an R value of 0.087. At this stage the observed structure factors were corrected for extinction, using the expression given by Zachariasen.[11] With the absorption term set equal to unity, and with observed intensities on an absolute scale, the value of the extinction parameter, C, was found to be 6.40×10^{-6}. Additional refinement on the parameters mentioned above lowered the R value to 0.059. Introduction of anisotropic thermal parameters for the atoms of the tetramethylammonium ion resulted in an R value of

Table 2. Anisotropic thermal parameters (Å²) in the form $\exp[-2\pi^2(h^2a^{-2}U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}+\cdots)]$. All values have been multiplied by 10^3. Standard deviations from the least squares refinement in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ag	82(1)	105(1)	105(1)	0	0	−7(1)
N(1)	114(9)	175(11)	160(12)	0	0	−72(10)
C(1)	90(9)	93(8)	93(8)	0	0	−17(8)
O(1)	112(7)	114(7)	155(8)	0	0	−21(7)
N(2)	91(7)	113(8)	160(10)	0	0	−20(8)
C(2)	78(8)	85(8)	118(10)	0	0	−2(8)
O(2)	94(7)	209(11)	209(12)	0	0	−52(8)
N(3)	62(5)	67(5)	62(5)	0	0	6(4)
C(3)	53(7)	256(18)	157(12)	0	0	22(8)
C(4)	113(19)	146(21)	68(13)	0	0	−30(12)
C(5)	179(18)	97(13)	162(20)	29(13)	−67(15)	−7(16)
C(6)	127(23)	113(22)	58(14)	0	0	8(16)
C(7)	147(22)	116(19)	212(31)	26(16)	94(22)	−15(20)

0.048. Another refinement cycle on the occupancy factors of the disordered atoms was carried out, no other parameters being refined in this cycle. In a final cycle, all positional and anisotropic thermal parameters were allowed to vary. No shift was greater than 0.012 times the standard deviation. The final R value, including non-observed reflections with $K|F_c|$ exceeding the observable limit, was 0.048. The final atomic coordinates and occupancy factors are listed in Table 1, the thermal parameters in Table 2, and the structure factors in Table 3.

Table 3. Observed and calculated structure factors (× 10). Unobserved reflections are indicated by a minus sign on $F(O)$ and included at the threshold values.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
0	0	2	807	858	6	0	9	207	206	2	1	4	511	460	8	1	10	54	-44	4	2	4	260	279
0	0	4	520	-495	6	0	10	60	-5	2	1	5	689	-691	8	1	11	-44	-44	4	2	5	483	480
0	0	6	719	-704	6	0	11	106	107	2	1	6	515	495	8	1	12	51	-53	4	2	6	321	316
0	0	8	504	-525	6	0	12	-45	11	2	1	7	125	114	9	1	1	248	-247	4	2	7	96	-101
0	0	10	-43	-44	6	0	13	-44	6	2	1	8	286	279	9	1	2	199	195	4	2	8	198	197
0	0	12	209	210	6	0	14	51	16	2	1	9	341	355	9	1	3	41	-53	4	2	9	270	-269
0	0	14	90	93	7	0	1	173	-163	2	1	10	49	-35	9	1	4	111	109	4	2	10	65	-60
0	0	16	-45	-4	7	0	2	550	-546	2	1	11	185	185	9	1	5	178	178	4	2	11	132	-133
1	0	1	1063	1265	7	0	3	-38	34	2	1	12	88	-77	9	1	6	88	77	4	2	12	61	-65
1	0	2	364	-450	7	0	4	498	-486	2	1	13	-41	9	9	1	7	132	129	4	2	13	-42	7
1	0	3	671	652	7	0	5	42	51	2	1	14	55	-49	9	1	8	50	-32	4	2	14	-44	-19
1	0	4	443	-428	7	0	6	80	-96	2	1	15	66	-59	9	1	9	-44	38	4	2	15	-46	21
1	0	5	805	-794	7	0	7	-38	-30	2	1	16	-46	-15	9	1	10	53	-50	5	2	1	194	-192
1	0	6	301	-301	7	0	8	152	145	3	1	1	886	-859	9	1	11	-45	-21	5	2	2	626	615
1	0	7	612	-604	7	0	9	73	71	3	1	2	559	-514	10	1	0	109	-135	5	2	3	69	60
1	0	8	141	131	7	0	10	194	195	3	1	3	186	-168	10	1	1	-40	30	5	2	4	505	512
1	0	9	151	-153	7	0	11	-44	41	3	1	4	558	-574	10	1	2	-41	-44	5	2	5	95	100
1	0	10	100	101	7	0	12	-45	39	3	1	5	507	491	10	1	3	188	191	5	2	6	91	84
1	0	11	163	174	7	0	13	-46	-18	3	1	6	253	-246	10	1	4	69	80	5	2	7	89	86
1	0	12	-41	6	8	0	0	203	-194	3	1	7	559	550	10	1	5	154	155	5	2	8	111	-113
1	0	13	136	139	8	0	1	277	-279	3	1	8	313	307	10	1	6	100	91	5	2	9	-38	32
1	0	14	-43	2	8	0	2	104	-112	3	1	9	105	108	10	1	7	-44	-18	5	2	10	163	-169
1	0	15	49	49	8	0	3	341	-346	3	1	10	207	211	10	1	8	-45	51	5	2	11	-41	3
1	0	16	-46	-7	8	0	4	67	68	3	1	11	-39	-35	10	1	9	69	-53	5	2	12	80	-66
2	0	0	641	703	8	0	5	112	-110	3	1	12	-40	19	10	1	10	-46	-9	5	2	13	-45	-23
2	0	1	605	-532	8	0	6	118	118	3	1	13	83	-84	11	1	1	60	-46	5	2	14	-46	28
2	0	2	660	662	8	0	7	51	52	3	1	14	-43	-25	11	1	2	110	120	6	2	0	92	-82
2	0	3	915	-939	8	0	8	118	116	3	1	15	-45	-19	11	1	3	-43	32	6	2	1	239	246
2	0	4	162	-164	8	0	9	164	171	4	1	0	625	-662	11	1	4	108	117	6	2	2	47	-47
2	0	5	230	-218	8	0	10	-43	24	4	1	1	288	-303	11	1	5	45	37	6	2	3	494	486
2	0	6	908	-857	8	0	11	81	91	4	1	2	589	-571	11	1	6	-45	28	6	2	4	117	119
2	0	7	38	32	8	0	12	47	-15	4	1	3	642	-656	11	1	7	60	42	6	2	5	345	347
2	0	8	321	-312	9	0	1	140	-134	4	1	4	210	210	11	1	8	-46	-35	6	2	6	40	13
2	0	9	66	58	9	0	2	115	-104	4	1	5	155	-159	12	1	0	56	-13	6	2	7	95	-96
2	0	10	73	74	9	0	3	-38	-38	4	1	6	447	449	12	1	1	-46	59	6	2	8	-38	15
2	0	11	136	135	9	0	4	217	-213	4	1	7	82	79	12	1	2	-44	-15	6	2	9	175	-174
2	0	12	150	155	9	0	5	115	113	4	1	8	286	279	12	1	3	89	86	6	2	10	-41	2
2	0	13	-42	0	9	0	6	-41	-3	4	1	9	140	135	12	1	4	-46	28	6	2	11	87	-83
2	0	14	89	81	9	0	7	150	166	4	1	10	-38	-12	12	1	5	72	57	6	2	12	-44	-11
2	0	15	-45	-35	9	0	8	111	128	4	1	11	109	114	0	2	0	2318	-2584	6	2	13	-45	-2
2	0	16	-46	12	9	0	9	-44	36	4	1	12	80	-85	0	2	2	721	-694	6	2	14	-46	-12
3	0	1	977	1037	9	0	10	82	76	4	1	13	-42	-3	0	2	4	221	235	7	2	1	119	122
3	0	2	393	-380	9	0	11	-45	-18	4	1	14	58	-63	0	2	6	541	537	7	2	2	387	394
3	0	3	-31	-57	10	0	0	113	-114	4	1	15	47	-35	0	2	8	389	389	7	2	3	-37	-33
3	0	4	548	-562	10	0	1	48	-39	5	1	1	763	-757	0	2	10	43	63	7	2	4	373	381
3	0	5	654	-659	10	0	2	102	-109	5	1	2	279	-274	0	2	12	157	-157	7	2	5	-37	-20
3	0	6	186	-180	10	0	3	177	-166	5	1	3	153	-148	0	2	14	92	-80	7	2	6	80	81
3	0	7	549	-568	10	0	4	53	68	5	1	4	236	-241	1	2	1	1185	-1134	7	2	7	-38	27
3	0	8	285	275	10	0	5	76	-66	5	1	5	389	388	1	2	2	612	552	7	2	8	112	-112
3	0	9	131	-127	10	0	6	118	118	5	1	6	-33	5	1	2	3	250	-267	7	2	9	52	-62
3	0	10	199	212	10	0	7	-43	32	5	1	7	471	463	1	2	4	316	311	7	2	10	157	-152
3	0	11	106	102	10	0	8	-45	57	5	1	8	168	159	1	2	5	641	626	7	2	11	-44	-34
3	0	12	79	65	10	0	9	63	55	5	1	9	90	96	1	2	6	195	196	7	2	12	-45	-34
3	0	13	104	112	10	0	10	-46	11	5	1	10	75	71	1	2	7	505	504	7	2	13	-46	15
3	0	14	-43	-18	11	0	1	152	-149	5	1	11	124	-115	1	2	8	118	-121	8	2	0	168	169
3	0	15	-45	33	11	0	2	97	-97	5	1	12	-41	26	1	2	9	121	113	8	2	1	222	228
3	0	16	-46	-33	11	0	3	-43	-15	5	1	13	77	-86	1	2	10	84	-91	8	2	2	94	94
4	0	0	287	280	11	0	4	51	-24	5	1	14	-44	-21	1	2	11	157	-153	8	2	3	269	276
4	0	1	613	-570	11	0	5	87	66	5	1	15	59	-31	1	2	12	-39	7	8	2	4	45	-53
4	0	2	334	341	11	0	6	-45	-15	6	1	0	998	-1035	1	2	13	97	-109	8	2	5	89	86
4	0	3	887	-883	11	0	7	98	96	6	1	1	-33	-22	1	2	14	-42	0	8	2	6	99	-105
4	0	4	334	-326	11	0	8	-46	25	6	1	2	380	-379	1	2	15	-44	-37	8	2	7	43	-38
4	0	5	611	-593	12	0	0	145	-155	6	1	3	-32	-11	2	2	0	529	-499	8	2	8	84	-90
4	0	6	373	-366	12	0	1	-46	-3	6	1	4	256	257	2	2	1	142	148	8	2	9	137	-134
4	0	7	113	100	12	0	2	66	-67	6	1	5	-35	-44	2	2	2	547	-525	8	2	10	-43	-14
4	0	8	252	-255	12	0	3	-44	-20	6	1	6	387	395	2	2	3	547	532	8	2	11	78	-73
4	0	9	353	342	12	0	4	-45	35	6	1	7	-36	26	2	2	4	129	133	8	2	12	-45	12
4	0	10	46	49	12	0	5	-46	-8	6	1	8	190	193	2	2	5	199	202	9	2	1	107	104
4	0	11	169	172	12	0	6	58	60	6	1	9	-39	22	2	2	6	697	693	9	2	2	80	80
4	0	12	34	77	0	1	1	533	-624	6	1	10	-40	7	2	2	7	-33	-3	9	2	3	-39	31
4	0	13	-43	-12	0	1	3	876	-837	6	1	11	-41	-9	2	2	8	231	237	9	2	4	187	182
4	0	14	-44	28	0	1	5	470	-491	6	1	12	117	-119	2	2	9	-35	-17	9	2	5	71	-85
4	0	15	-45	-26	0	1	7	213	216	6	1	13	-44	-37	2	2	10	44	-56	9	2	6	-41	2
5	0	1	351	358	0	1	9	545	546	6	1	14	75	-73	2	2	11	117	-114	9	2	7	118	-126
5	0	2	818	-819	0	1	11	188	186	7	1	1	456	-465	2	2	12	123	-123	9	2	8	103	-107
5	0	3	231	-211	0	1	13	-40	10	7	1	2	43	-30	2	2	13	-41	-10	9	2	9	-44	-32
5	0	4	731	-732	0	1	15	59	-49	7	1	3	69	-66	2	2	14	78	-66	9	2	10	-45	-60
5	0	5	126	-125	1	1	1	418	-347	7	1	4	128	131	2	2	15	-45	30	9	2	11	-45	15
5	0	6	77	-89	1	1	2	1366	-1400	7	1	5	276	282	3	2	1	694	-696	10	2	0	115	103
5	0	7	131	-127	1	1	3	888	872	7	1	6	-37	7	3	2	2	495	479	10	2	1	-41	39
5	0	8	173	167	1	1	4	1237	-1216	7	1	7	204	210	3	2	3	-29	42	10	2	2	85	83
5	0	9	42	-41	1	1	5	-27	23	7	1	8	76	-86	3	2	4	435	426	10	2	3	135	126
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5	0	11	-44	7	1	1	7	65	62	7	1	10	-42	43	3	2	6	125	121	10	2	5	73	69
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5	0	14	-45	-35	1	1	10	355	351	7	1	13	71	-77	3	2	9	118	117	10	2	8	-45	-46
5	0	15	50	-10	1	1	11	-38	-19	8	1	0	402	-387	3	2	10	177	-180	10	2	9	-45	-43
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6	0	1	272	-278	1	1	13	49	-53	8	1	2	219	-223	3	2	12	-41	-44	11	2	2	83	80
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6	0	5	449	-449	2	1	0	88	70	8	1	6	262	270	4	2	0	419	-418	11	2	6	-44	9
6	0	6	-37	-45	2	1	1	611	-581	8	1	7	-41	32	4	2	1	347	333	11	2	7	76	-79
6	0	7	94	107	2	1	2	493	-480	8	1	8	150	140	4	2	2	266	-264	12	2	0	125	125
6	0	8	-37	-5	2	1	3	1284	-1352	8	1	9	-43	-53	4	2	3	687	667	12	2	1	-45	-1

Table 3. Continued.

H	K	L	F(O)	F(C)
12	2	2	-46	53
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12	2	4	-45	-27
0	3	1	548	515
0	3	3	624	607
0	3	5	306	310
0	3	7	130	-127
0	3	9	373	-379
0	3	11	111	-118
0	3	13	-42	4
0	3	15	-45	31
1	3	1	99	97
1	3	2	648	648
1	3	3	348	-321
1	3	4	680	670
1	3	5	-31	-15
1	3	6	60	63
1	3	7	-34	-4
1	3	8	177	-170
1	3	9	71	-66
1	3	10	193	-203
1	3	11	-39	1
1	3	12	91	-87
1	3	13	-42	35
1	3	14	45	34
1	3	15	-45	10
2	3	0	272	259
2	3	1	360	349
2	3	2	257	257
2	3	3	744	747
2	3	4	230	-235
2	3	5	400	403
2	3	6	330	-330
2	3	7	74	-69
2	3	8	183	-184
2	3	9	217	-221
2	3	10	50	50
2	3	11	115	-115
2	3	12	-42	56
2	3	13	-43	-5
2	3	14	-44	29
2	3	15	-46	39
3	3	1	437	419
3	3	2	321	336
3	3	3	138	152
3	3	4	401	397
3	3	5	281	-282
3	3	6	151	142
3	3	7	276	-276
3	3	8	199	-207
3	3	9	69	-76
3	3	10	133	-139
3	3	11	-40	11
3	3	12	-42	-7
3	3	13	55	56
3	3	14	-44	16
4	3	0	510	515
4	3	1	166	160
4	3	2	230	286
4	3	3	327	322
4	3	4	141	-136
4	3	5	65	78
4	3	6	262	-256
4	3	7	-37	-31
4	3	8	187	-191
4	3	9	71	-67
4	3	10	-40	11
4	3	11	86	-77
4	3	12	70	57
4	3	13	-43	-2
4	3	14	50	40
5	3	1	430	445
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5	3	3	118	116
5	3	4	156	146
5	3	5	266	-273
5	3	6	-36	-8
5	3	7	308	-303
5	3	8	109	-110
5	3	9	-40	-53
5	3	10	65	-55
5	3	11	79	74
5	3	12	-43	-13
5	3	13	62	55
6	3	0	541	548
6	3	1	37	-20
6	3	2	225	227
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6	3	4	156	-156
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6	3	6	235	-235
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6	3	8	111	-121
6	3	9	-41	-12
6	3	10	-41	-12
6	3	11	-43	6
6	3	12	71	74
6	3	13	-45	22
7	3	1	300	305
7	3	2	-37	16
7	3	3	-37	19
7	3	4	94	-94
7	3	5	182	-178
7	3	6	-38	-1
7	3	7	146	-151
7	3	8	44	55
7	3	9	-42	-33
7	3	10	-43	23
7	3	11	59	55
7	3	12	-45	16
8	3	0	234	230
8	3	1	69	-64
8	3	2	147	147
8	3	3	74	-77
8	3	4	41	-11
8	3	5	-40	-2
8	3	6	170	-169
8	3	7	-42	-25
8	3	8	93	-90
8	3	9	-44	31
8	3	10	-44	25
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9	3	2	116	-121
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10	3	8	-46	-29
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11	3	4	73	-71
11	3	5	-46	-22
11	3	6	-47	-18
0	4	0	1010	995
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1	4	6	95	-109
1	4	7	275	-288
1	4	8	62	56
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1	4	10	44	52
1	4	11	67	76
1	4	12	-43	-3
1	4	13	56	58
1	4	14	-46	0
2	4	0	274	274
2	4	1	142	-137
2	4	2	233	235
2	4	3	256	-252
2	4	4	92	-91
2	4	5	60	-52
2	4	6	307	-309
2	4	7	-38	7
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2	4	13	-44	4
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4	4	5	204	-207
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4	4	12	-44	34
4	4	13	-45	-4
5	4	1	111	101
5	4	2	307	-312
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5	4	7	-39	-25
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5	4	9	-41	-16
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6	4	7	-41	44
6	4	8	-41	-8
6	4	9	94	90
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6	4	11	-46	47
6	4	12	47	5
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7	4	2	201	-203
7	4	3	-39	9
7	4	4	183	-180
7	4	5	-40	13
7	4	6	-41	-44
7	4	7	-41	-10
7	4	8	74	57
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8	4	2	42	-48
8	4	3	148	-145
8	4	4	-41	17
8	4	5	-42	-52
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8	4	9	63	70
9	4	1	56	-58
9	4	2	45	-41
9	4	3	50	-11
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10	4	4	-45	31
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2	5	3	276	-276
2	5	4	-38	26
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2	5	6	117	123
2	5	7	-40	38
2	5	8	60	63
2	5	9	93	82
2	5	10	-43	-9
2	5	11	54	47
2	5	12	-45	-19
3	5	1	196	-201
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3	5	3	-38	-24
3	5	4	149	-149
3	5	5	119	112
3	5	6	46	-64
3	5	7	108	102
3	5	8	79	70
3	5	9	-43	32
3	5	10	63	58
3	5	11	-44	-16
3	5	12	-45	4
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6	5	2	107	-95
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6	5	9	-45	13
6	5	10	-46	0
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7	5	2	-41	-8
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7	5	6	-43	6
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7	5	8	-44	-17
7	5	9	-45	17
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8	5	1	-43	33
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9	5	1	87	-70
9	5	2	-45	46
9	5	3	-44	-12
9	5	4	-45	37
9	5	5	-47	50
10	5	0	-46	-32
0	6	0	300	-307
0	6	2	95	-97
0	6	4	72	66
0	6	6	85	92
0	6	8	77	75
0	6	10	-45	2
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1	6	2	45	41
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3	6	1	118	-115
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3	6	8	45	-32
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4	6	0	57	-50
4	6	1	50	57
4	6	2	42	-40
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4	6	9	-47	-57
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6	6	1	-44	24
6	6	2	-43	-5
6	6	3	85	80
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6	6	5	53	55
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6	6	7	-46	-11
7	6	1	-45	24
7	6	2	74	71
7	6	3	-45	2
7	6	4	71	64
7	6	5	-46	-9
8	6	0	-46	30
8	6	1	56	34
8	6	2	-46	13
8	6	3	-47	51
0	7	1	-43	35
0	7	3	57	60
0	7	5	59	26
0	7	7	-46	-15
1	7	1	-43	19
1	7	2	86	72
1	7	3	-44	-24
1	7	4	59	65
1	7	5	-44	-3
1	7	6	-45	14
1	7	7	-45	-5
2	7	0	-43	17
2	7	1	53	27
2	7	2	-44	23
2	7	3	67	73
2	7	4	-44	-14
2	7	5	52	40
2	7	6	-46	-30
2	7	7	-45	-9
3	7	1	62	51
3	7	2	-44	33
3	7	3	51	17
3	7	4	-45	42
3	7	5	-45	-29
3	7	6	-46	17
4	7	0	-46	62
4	7	1	51	27
4	7	2	-45	28
4	7	3	-46	35
4	7	4	-46	-17
4	7	5	-46	11
5	7	1	-46	42
5	7	2	-45	14
5	7	3	-46	13
5	7	4	-46	13

An electron density map, with phases based on the final parameters, was calculated. The electron densities (e/Å^3) in the atomic positions had the values, 51.6 for Ag; 4.1 for N(1); 4.9 for C(1); 5.7 for O(1); 4.7 for N(2); 4.7 for C(2); 4.5 for O(2); 7.6 for N(3); 4.3 for C(3); 2.6 for C(4); 2.3 for C(5); 2.3 for C(6); and 1.9 for C(7). The last four atoms are the disordered methyl carbon atoms. It was not possible, on the basis of the electron density map, to distinguish between the atoms of the isocyanate groups. The areas of highest electron density in a final dif-

Table 4. Bond lengths (Å) and angles (°). Standard deviations, in parentheses, have been calculated from those of Table 1, without regard to coordinate covariances and errors in unit cell dimensions. A prime denotes an atom generated by a mirror plane.

Ag–N(1) = 2.015(13)	∠N(1)–Ag–N(2) = 177.2(5)
Ag–N(2) = 2.068(12)	∠Ag–N(1)–C(1) = 170.0(13)
N(1)–C(1) = 1.076(19)	∠Ag–N(2)–C(2) = 172.1(12)
N(2)–C(2) = 1.111(18)	∠N(1)–C(1)–O(1) = 178.2(16)
C(1)–O(1) = 1.200(17)	∠N(2)–C(2)–O(2) = 179.8(17)
C(2)–O(2) = 1.129(18)	∠C(3)–N(3)–C(4) = 107.2(11)
N(3)–C(3) = 1.456(14)	∠C(3)–N(3)–C(5) = 106.7(10)
N(3)–C(4) = 1.53(3)	∠C(4)–N(3)–C(5) = 112.2(10)
N(3)–C(5) = 1.43(3)	∠C(5)–N(3)–C(5′) = 111.4(14)
N(3)–C(6) = 1.58(3)	∠C(3)–N(3)–C(6) = 110.8(13)
N(3)–C(7) = 1.47(3)	∠C(3)–N(3)–C(7) = 104.2(15)
	∠C(6)–N(3)–C(7) = 111.0(16)
	∠C(7)–N(3)–C(7′) = 113.0(11)

ference Fourier summation were located near the disordered methyl carbon atoms. The maximum peak height in this map was 0.38 e/Å³. No attempts were made to locate the hydrogen atoms. On the basis of the successful refinement, it was concluded that the correct space group is *Pnma*.

RESULTS

Thermal motion. The thermal parameters of all atoms except the nitrogen atom of the tetramethylammonium ion [N(3)] have unusually high and strongly anisotropic values (Table 2). It was thought reasonable to analyze the thermal motions of the diisocyanatoargentate(I) ion in terms of the rigid-body tensors of translation (**T**), libration (**L**), and screw motion (**S**), according to Schomaker and Trueblood.[8] The results of the analysis, however, indicated that the rigid-body assumption was not applicable. The root mean square discrepancy between the observed U_{ij} values and the values calculated from the rigid-body model was 0.020 Å², indicating a considerable internal motion. Moreover, the eigenvalue of one of the libration axes was negative. Further results of the analysis are therefore not reported.

Due to the disorder of the methyl carbon atoms of the tetramethylammonium ion, and hence the large standard deviations of the corresponding thermal parameters, a similar rigid-body thermal analysis of this ion was not attempted.

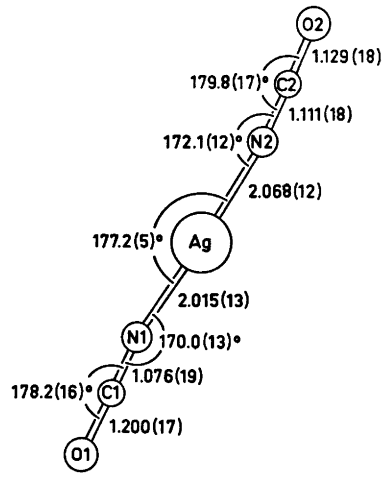

Fig. 1. The diisocyanatoargentate ion as seen along the normal to the mirror plane.

The diisocyanatoargentate(I) ion. The bond lengths and angles are given in Table 4. The structure analysis did not provide a determination of whether the silver atom is nitrogen-bonded or oxygen-bonded. From the earlier studies [2,3] it can be concluded that both ligands are bonded to the silver atom through the nitrogen atoms, and this has been presupposed throughout the present crystal structure determination.

All the atoms of the ion are located in a crystallographic mirror plane. A drawing of the diisocyanatoargentate(I) ion, as seen along the

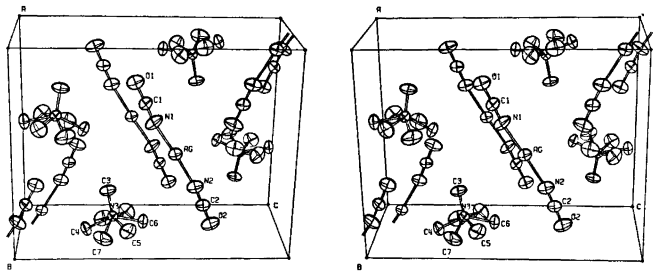

Fig. 2. A stereoscopic pair of drawings, with 20 % probability ellipsoids, showing the content of one unit cell. The labelled atoms of the diisocyanatoargentate ion are at $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$ relative to Table 1. Both sets of positions for the disordered methyl carbon atoms of the tetramethylammonium ions have been included.

normal to this plane, is shown in Fig. 1. The ion is approximately linear, with the largest deviations from linearity occurring in the Ag – N – C angles. The isocyanate groups do not deviate significantly from linearity, and the deviation of the N – Ag – N angle from 180° is rather small.

The standard deviations in bond lengths, as calculated from the least squares values, are probably too small. An adequate thermal analysis would most likely imply rather large corrections in bond lengths. If corresponding bond lengths from opposite sides of the silver atom are compared, they are seen to differ to some extent. The sum of bond lengths within the Ag – N(1) – C(1) – O(1) part of the ion is 4.291 Å, while the sum for the Ag – N(2) – C(2) – O(2) part is 4.308 Å. The average values for the bond lengths are: Ag – N = 2.042 Å, N – C = 1.094 Å, and C – O = 1.165 Å. The Ag – N bond lengths may be compared with the corresponding bond length, 2.115(18) Å, in silver isocyanate, AgNCO.[12] In the crystals of the latter compound there are zigzag chains, with alternating silver and nitrogen atoms, the nitrogen atoms being sp^2 hybridized ($\angle$Ag – N – C = 128.2°), rather than *sp* hybridized as in the diisocyanatoargentate(I) ion. In silver thiocyanate, AgSCN, the nitrogen atom seems to be *sp* hybridized, with an Ag – N bond length of 2.223(28) Å.[13] In this compound, a sulphur atom is bonded to the silver atom approximately opposite to the nitrogen atom.

The tetramethylammonium ion. The space group *Pnma* requires that the tetramethylammonium ion possesses mirror plane symmetry, with the nitrogen atom and two methyl carbon atoms located in the mirror plane. The bond lengths and angles are listed in Table 4, and the shape of the ion appears from Fig. 2. Three methyl carbon atoms of the tetramethylammonium ion are disordered. With a prime denoting an atom generated by the mirror plane, they are labelled C(4), C(5), and C(5′) in one set of positions. From these positions, the other ones are generated by rotating the entire ion approximately 60° about the N(3) – C(3) bond. The atoms in the other set are then C(6), C(7), and C(7′). In Fig. 2 both sets of positions have been included. The large thermal parameters might indicate that the disorder is due to extreme thermal motion, with the ion rotating more or less freely about the N(3) – C(3) bond. It appears more plausible, however, that there is a statistical distribution of ions in two different orientations, and that transition from one orientation to the other is not possible.

The tetramethylammonium ion is approximately tetrahedral. Due to the disorder, the derived bond lengths and angles are rather inaccurate, but the values are within the normal range.

Crystal packing. A stereoscopic drawing of the cell content is shown in Fig. 2. There are no particularly short non-bonding distances. The shortest distances from the silver atom to atoms of different ions involve isocyanate nitrogen and oxygen atoms. One silver-oxygen distance is 3.29(2) Å, with the oxygen atom [O(2)] located in the same mirror plane as the silver atom. Two equivalent silver-nitrogen distances are 3.552(5) Å, with the nitrogen atoms [N(1)] located in mirror planes $\pm b/2$ from the mirror plane con-

taining the silver atom. The silver atom and its three non-bonded neighbours just mentioned are positioned approximately in a plane normal to the silver-nitrogen bond directions.

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